Extending the Limits of Oxygen Delignification

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O Delignification

N. American Bleach Plants

Improved environmental and operating cost performance
O Delignification

Increased interest in one and two-stage oxygen delignification

Yield and Operating Benefits
O Delignification: Background

Literature

- 1960/70s
  - basic engineering & chemistry
- 1980/early 90s
  - process parameters, energy, environmental, pretreatments, fundamental chemistry, pulp properties
- Late 1990’s
  - yield, selectivity, process parameters, lignin/carbohydrate chemistry, catalysts
Fundamentals of Oxygen Delignification
O Delignification: Background

Free Phenolic

Fragmented Lignin

Acid & ketone groups
O Delignification: Background

Several potential bleaching agents with varying sensitivities to reactions with transitional metals
O Delignification: Background

Free Phenolic

Chain Fragmented Lignin
O Delignification: Lignin Structure Studies

“Oxygen delignification leads to a decrease of various types of phenolic groups in residual lignin. However, condensed phenolics survived...to a large extent” Jiang & Argyropoulos, JPPS, 1999.


“After the oxygen stage, the isolated residual lignin seems to have a somewhat more intact and less oxidized structure than the corresponding lignin from the unbleached pulp.” Gellerstedt, Heuts, & Robert, JPPS, 1999.

Discrepancies exist between model compound and residual lignin studies
Delignification Results

(E+O)D(E+O)
O Delignification Studies

Research Objectives

• Examine O bleachability
• High & Low kappa SW kraft
• Determine
  – Physical properties
  – Fundamental lignin structures

• Contribute to future O-delignification road map to improve performance
O Delignification: Experimental Design

<table>
<thead>
<tr>
<th>SW Kraft Pulps</th>
<th>Bleach Sequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>High kappa pulp</td>
<td>O</td>
</tr>
<tr>
<td>- 56.2</td>
<td>OO</td>
</tr>
<tr>
<td>Low kappa pulp</td>
<td>(E+O)D_{kf:0.05}(E+O)</td>
</tr>
<tr>
<td>- 26.6</td>
<td></td>
</tr>
</tbody>
</table>
## Experimental Conditions: Low Kappa Pulp

<table>
<thead>
<tr>
<th>Stage</th>
<th>O-Pres./psi</th>
<th>% NaOH</th>
<th>O-Temp./C</th>
<th>O-Time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>80</td>
<td>1.5, 2.5, 3.5</td>
<td>105</td>
<td>80</td>
</tr>
<tr>
<td>OO (i)</td>
<td>130</td>
<td>1.5, 2.5, 3.5</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>(ii) 60</td>
<td></td>
<td></td>
<td>105</td>
<td>60</td>
</tr>
<tr>
<td>(E+O)D(E+O)</td>
<td>80</td>
<td>1.5, 2.5, 3.5</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

MgSO₄: 0.30%, 12% csc

High kappa pulp: same conditions except % NaOH: 2.5, 4.1, 5.8
O-Delignification: Low Kappa

- BS
- NaOH: 1.5%
- NaOH: 2.5%
- NaOH: 3.5%

Kappa #
O-Delignification: High Kappa

![Bar chart showing Kappa values for different treatments: BS, NaOH:2.5, NaOH:4.1, NaOH:5.8, (E+O)D(E+O), O, OO. The y-axis represents Kappa # ranging from 20 to 60, and the x-axis represents different treatments.]
O-Delignification: Bleachability

Delignification
Low Kappa (LK)
OO ≈ O
High Kappa (HK)
OO > O

*Δ kappa/charge of NaOH
O-Delignification: Viscosity

- Low Kappa BS L-1.5%
- L-2.5%
- L-3.5%
- High Kappa BS H-2.5%
- H-4.1%
- H-5.8%

Viscosity/°cP

- BS
- O
- OO
- (E+O)D(E+O)
O-Delignification: Conclusions

• Oxygen delignification of low kappa SW kraft pulp
  – % delignification comparable for O & OO
  – OO improved viscosity
  – low NaOH charge yielded best % delignification
  – (E+O)D(E+O) performance ~15-30% O

• Oxygen delignification of high kappa SW kraft pulp
  – OO improved delignification
  – OO improved viscosity
  – higher charges of NaOH less effective
Go
No-Go
Chemistry
Contributing to
O & OO
Fundamental Pulp Properties
Controlling Oxygen Bleachability

Procedure

• Isolate lignin from:
  – Brownstocks
  – O and OO pulps
  – Effluents

• Establish lignin structure using advanced NMR techniques.
Lignin Structure of Brownstock

**$^{13}$C NMR Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Low Kappa</th>
<th>High Kappa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Ph</td>
<td>3.00</td>
<td>1.00</td>
</tr>
<tr>
<td>β-O-4</td>
<td>0.84</td>
<td>1.00</td>
</tr>
<tr>
<td>Condensed Ar-R</td>
<td>1.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Ar-OMe</td>
<td>0.91</td>
<td>1.00</td>
</tr>
<tr>
<td>Acids</td>
<td>1.82</td>
<td>1.00</td>
</tr>
</tbody>
</table>

[Chemical structures for CH$_2$Ph, β-O-4, and Ar-OMe with R: H or C]
Non-Condensed Phenolics in Brownstock, O, and OO Pulps

Mid point charge of NaOH for O and OO

![Chemical structure](image)
Mid point charge of NaOH for O and OO
Acids and Aliphatic Hydroxyl Groups in Brownstock, O, and OO Pulps

Residual lignin is oxidized
No side chain oxidation
Analysis of Bleach Effluents
Loss of Phenolics: Low Kappa Pulp

Condensed phenolics resistant to O or OO

% Change in Phenolic Content*

file: Non C5 Condensed Phenolics
file: C5 Condensed Phenolics

1.5% NaOH Convent. O
3.5% NaOH Convent. O
3.5% NaOH OO

*%: \([\text{Effluent PhOH}] - [\text{Brownstock PhOH}] / [\text{Brownstock PhOH}]\)
Change in $p$-Phenolics for High and Low Kappa Pulps

Previously unreported resistant to Ox.

Approx. 11% conc. of non-condensed PhOH in Brownstock
Conclusions
O - Delignification: Lignin Results

- Primary site of oxidation is unsubstituted phenolics
- Substituted phenols resistant to oxidation
- Side chain oxidation is not a dominant O-reaction

- Lignin structure enriched in acid groups
- $p$-Hydroxyl phenyls may act as blocking groups to O or OO chemistry
O - Delignification: Implications

- Enhanced O-stages must activate both condensed and unsubstituted PhOHs.
- Need new chemistry for condensed phenoxy and p-hydroxy phenyl groups.
- Biotechnology opportunities
- High and low kappa pulps behave differently toward O and OO
IPST Member Companies
U.S. Department of Energy
Cooperative Agreement
DE-FC07-00ID13870

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